EFFECT OF TEMPERATURE ON THE SYNTHESIS OF CERIUM CHALCOGENIDES

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ABSTRACT FINAL REPORT NObs 77068

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The purpose of ~~this~~ investigation was to develop an isothermal study for the cerium-sulfur compositions synthesized over the temperature range of 600°C to 1300°C in 25 degree increments.

Cerium sulfide compounds were synthesized under a carbon disulfide atmosphere from ceria (CeO_2) in a carbon combustion tube furnace. The furnace was designed specifically for this investigation as a continuous duty unit featuring close temperature control and has proven to be an effective research tool. The chemical analyses of the cerium sulfide compounds were determined by the analytical procedures compiled in Appendix A. The crystal structures were studied by X-ray diffraction techniques using filtered chromium K alpha radiation.

The experimental procedure developed for synthesizing cerium sulfide compounds in a carbon disulfide atmosphere is discussed in detail. A complete description is given for the construction of the carbon combustion tube furnace. The wet chemistry results are documented for 35 cerium sulfide compounds prepared under isothermal conditions over the temperature range of 600°C to 1300°C. A comparison of the wet chemical results reported by two independent laboratories for the same sulfide samples is also given in tabular form. From

the wet chemistry data, a partial binary diagram ~~has been~~ proposed for the cerium-sulfur system. The amount of the oxide converted to a surfide for the 600°C to 1300°C temperature region is illustrated graphically. A limited amount of density data is presented in graphical form. X-ray diffraction data for the cerium sulfide compounds are tabulated in Appendix B. The original X-ray diffraction traces are reproduced for a graphical comparison of the sulfide phases.

Cerium dissolves 25 per cent sulfur at 1300°C and 27 per cent at 1115° C, forming a Th_3P_4 type body-centered cubic structure. Complex X-ray diffraction spectra were obtained for the cerium sulfide compounds prepared below 1100°C. From 950°C to 1100°C, two cubic phases have been indexed as follows: a body-centered cubic Ce_3S_4 type structure with an a_o value of 8.65 A being the predominant phase, the second phase is simple cubic with an a_o value of 8.85 A.

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I INTRODUCTION - STATEMENT OF PROBLEM

In recent years there has been considerable interest in the possibility of using the cerium sulfide compounds for high temperature and thermoelectric materials. Their high melting points (2000°C) and low dissociation pressures make these compounds attractive for many current and potential applications in science and industry.

Cerium monosulfide, CeS, with an ionic valence of +3, has metallic characteristics. Cerium sesquisulfide, Ce_2S_3, exhibits ordinary refractory properties in its affinity for oxygen and water and its electrical insulator characteristics. Cerium can also combine with the chalcogenide, sulfur, to form three other known sulfides; namely, cerium disulfide, CeS_2, Ce_3S_4, and cerium black, which is a solid solution of Ce_2S_3 in Ce_3S_4. Unfortunately, the complete binary phase diagram for the cerium-sulfur system has not been published to date. In fact, much confusion still exists concerning the number of cerium sesquisulfide (Ce_2S_3) allotropes and their transformation temperatures.

Eastman et al.[(1)*] and Flahaut and Guittard[(2)] have found indications that more than one phase exists for the sesquisulfide compound, Ce_2S_3. The alpha phase, which had been previously formed by the dissociation of CeS_2

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*Parenthetical references placed superior to the line of text refer to the Bibliography.

below 900°C, was transformed to the beta phase on subsequent heating above 1100°C. The beta phase was synthesized at temperatures below 1100°C but did not transform to the gamma phase when annealed at temperatures above 1100°C and remained metastable at the lower temperatures. The phase problem becomes considerably more complex, however, if one wishes to examine the crystallographic configurations of the cerium sesquisulfide allotropes. The gamma phase has been indexed by Zachariasen[3] as a defect body-centered cubic structure. The alpha and beta phases have not been indexed because of their complex X-ray diffraction spectra. The results of this study indicated that the limited information available on this subject is undoubtedly due to the difficulty of preparing high purity cerium sesquisulfide (Ce_2S_3) without incurring oxygen contamination.

The primary reason for the current interest in the cerium-sulfur compounds is to obtain high purity Ce_2S_3 for future thermoelectric studies. In view of its complex nature, it is not surprising that high purity Ce_2S_3 is not available commercially. Obviously, before proceeding with the processing of this material in the laboratory, more detailed information was needed regarding the temperature-chemistry correlation. For these reasons, a systematic approach had to be undertaken to determine the basic temperature and chemistry parameters for the cerium-sulfur system.

Consequently, the investigation described in this thesis was initiated to determine the influence of the reaction temperature on the resultant X-ray

diffraction spectra and chemistry of the process. In this study, the preparation and properties of the cerium sulfide compounds are described over the temperature range of 600°C to 1300°C.

II LITERATURE SURVEY

The rare earth element cerium, belonging to group 3 of the Periodic Table of Elements and the first member of the 4f-transition group, has an atomic weight of 140.13. Its atomic number is 58 and its atomic radius in the gamma form is 1.82 angstroms. As a divalent element with a valency of +3 or +4, it readily forms colorless cerous salts or yellow-orange ceric salts. The +4 valency for cerium is characteristic for this element. Cerium gives up its only 4f electron and acquires the structure of lanthium +3.

The two oxides of cerium are the unstable basic anhydride, cerous oxide (Ce_2O_3) and the stable ceria, ceric oxide (CeO_2). These compounds are usually prepared by the decomposition of cerium oxalate or cerium nitrate. An oxysulfide, Ce_2O_2S, and four sulfides, CeS, Ce_3S_4, Ce_2S_3 and CeS_2 can be formed under suitable conditions.

The theoretical chemical compositions of the oxides, oxysulfides, and sulfides of cerium are compared on a weight per cent basis in Table I. The crystallographic properties of these oxidation products are summarized in Table II.

Zachariasen[3] identified the structure of gamma Ce_2S_3 as a defect body-centered cubic lattice containing 10-2/3 cerium atoms and 16 sulfur atoms. Every ninth metal site is vacant. If all 12 metal sites had been filled, the chemical composition would have been Ce_3S_4. Eastman et al.[6]

TABLE I

THEORETICAL CHEMICAL COMPOSITIONS OF CERIUM OXIDES AND SULFIDES

Compound	Molecular Weight	Cerium (W%)	Oxygen (W%)	Sulfur (W%)
Ce_2O_3	329.26	62.49	37.51	-----
CeO_2	172.13	81.41	18.59	-----
Ce_2O_2S	344.32	81.40	9.29	9.31
CeS	172.19	81.38	-----	18.62
Ce_3S_4	548.63	76.63	-----	23.37
Ce_2S_3	376.44	74.45	-----	25.55
CeS_2	204.25	68.61	-----	31.39
Cerium Black	925.07	75.38	-----	24.62

TABLE II

CRYSTALLOGRAPHIC PROPERTIES
OF CERIUM OXIDES AND SULFIDES

	Compound	System and Structure	a_o (A)	c_o (A)
*	CeS	Cubic, NaCl	5.76	
**	Ce_3S_4	BCC	8.625	
***	Cerium Black	BCC	8.630	
*	Ce_2S_3	BCC, Th_3P_4	8.6345	
****	CeS_2	Cubic	8.12	
*	Ce_2O_2S	Hex.	4.01	6.83
*****	Ce_2O_3	Hex.	3.88	6.06
*	CeO_2	FCC	5.411	

* ASTM Standard X-Ray Diffraction Patterns

** Zachariasen[3]

*** Eastman et al.[1]

**** Picon[4]

***** Davey[5]

reported that the low temperature (alpha and beta) phases of Ce_2S_3 have very complex structures which could possibly be attributed to a very low oxygen content. These structures have not been indexed to date. Carter[7] grew single crystals of Ce_2S_3 (about 0.1 mm on an edge) by a vapor transport method and obtained a lattice parameter of 8.59 A.

Carter[7] pictures CeS as a metallic compound in which each cerium atom forms two bonds distributed among its six neighboring sulfur atoms and a single metallic bond distributed among the next 12 nearest cerium atoms. This concept gives a total valency of approximately three.

Zachariasen[8] indexed cerium oxysulfide as a hexagonal compound similar in structure to Ce_2O_3. He further states that if a sulfur atom is substituted for one of the three oxygen atoms, together with a corresponding distortion of the resulting structure, an oxysulfide of cerium would be formed.

Carter[7] pointed out that the structure of CeS_2 could be tetragonal instead of cubic, in which the lattice parameters are nearly equal.

In 1901 Sterba[9] suggested that ceric sulfide (Ce_2S_3) could be produced by heating ceria (CeO_2) at an elevated (red hot) temperature in a hydrogen sulfide atmosphere. Blitz[10] reported in 1908 that CeS_2, formed from the reaction of cerium sulfate with hydrogen sulfide gas below 700°C, will dissociate at 755°C producing Ce_2S_3 and free sulfur. Klemm, et al.[11] in 1930, found that cerium sulfate heated to 1000°C in a hydrogen sulfide

atmosphere was converted directly to a Ce_2S_3 compound, having a very complex X-ray pattern. Picon[4] synthesized pure ceric sulfide (Ce_2S_3) at 1550°C in 1931.

In 1950 Eastman et al.[1] prepared cerium sesquisulfide (Ce_2S_3) by reacting ce ia (CeO_2) in a graphite container with hydrogen sulfide gas at 1200 °C to 1400°C for two to three hours. They postulated that the cerium sesquisulfide reaction would proceed by way of the oxysulfide. It was further stated that the cerium sesquisulfide reaction would not go to completion in a porcelain tube or a sulfur gas atmosphere, but that small amounts of oxygen contamination would change the cubic Th_3P_4 structure of Ce_2S_3 to a very complex structure.

In 1956, Flahaut and Guittard[2] substantiated the existence of three crystallographic forms of cerium sesquisulfide (Ce_2S_3). They indicated that perfectly dry H_2S and carbon boats were a necessity for the transformation of CeO_2 to Ce_2S_3. Banks et al.[12], in 1952, employed molten salts in an attempt to remove the oxides from the complex oxysulfide phases of cerium. Their results are compared by means of X-ray diffraction traces over a three degree range of two theta angles.

In 1959, during a private discussion with the writer, Carter[13] proposed a method for producing Ce_2S_3 at low temperatures by using a carbon disulfide atmosphere instead of hydrogen sulfide. Eastman et al.[6] and Flahaut and Guittard[2] suggested the possibility of the Ce_2S_3 reaction proceeding by way of the CeS or CeS_2 intermediate step.

Later, Carter [7], in his investigation of the rare earth chalcogenides, reported that Ce_2S_3 could be prepared in an hour from CeO_2 by using carbon disulfide and a carrier gas at 700°C to 860°C. Cerium sesquisulfides were also prepared from the cerium hydride. Appel et al. [14] have also produced gamma Ce_2S_3 from CeO_2 above 1500°C using H_2S as the sulfurizing agent.

Blitz [10] indicated that anhydrous cerium sulfate, when heated below 700°C in a hydrogen sulfide atmosphere, would produce CeS_2 with a slight amount of retained oxygen. Flahaut and Guittard [2] found that CeS_2 was produced when gamma Ce_2S_3, mixed with excess dry sulfur, was sealed in a tube and heated to 600°C. Carter [7] prepared CeS_2 from a mixture of cerium hydride and sulfur heated slowly from 350°C to 600°C. The excess sulfur was then distilled off at 400°C.

Eastman et al. [1] obtained CeS by heating the hydride with Ce_2S_3 at 2200°C. Flahaut and Attal [15] produced CeS by reacting cerium oxysulfide with Ce_3S_4 at 1650°C. After four hours, only 60 per cent of the material was transformed to CeS. The reduction of the reactants to CeS with an aluminum addition was complete after two hours at 1200°C in a vacuum. The alumina was subsequently removed by annealing at 1850°C under reduced pressure.

Eastman et al. [6] and Flahaut and Attal [15] have reported finding Ce_2O_2S by incomplete sulfurization of CeO_2. Flahaut and Attal [15] mention another method for making the oxysulfide. Hydrogen, saturated with water

vapor, was passed over the sulfide at 500°C. Cerous oxide (Ce_2O_3) would be formed if this reaction were allowed to go to completion.

III EXPERIMENTAL PROCEDURE OR TECHNIQUE

The high purity ceria (99.9 + per cent CeO_2) used in this investigation was procured from the Lindsay Chemical Division of the American Potash and Chemical Company. The average particle size of the material, as received, was less than 325 mesh. Results from a spectrochemical analysis of the ceric oxide as documented in Table III indicate that only traces of the other rare earth elements were present. However, the presence of a small amount of a cerous oxide phase (Ce_2O_3) has been detected from an X-ray diffraction examination of the material. The X-ray diffraction results are indexed in Table IV. The calculated a_o value of 11.39 A for the cerous phase agrees closely with the lattice parameters (a_o = 11.26 A) reported by Courtel and Loriers[16] in 1950. The reagent grade of chemically pure carbon disulfide was supplied by the Fisher Scientific Company.

Since Carter[13] had suggested that carbon disulfide might be used as the chalcogenide gas if a feasible experimental technique could be developed, an experimental procedure was developed during this study for the synthesis of cerium sulfide compounds as described in detail in the following text.

Figure 1 shows a schematic flow diagram of the experimental apparatus. The high purity ceric oxide powder was converted to a sulfide by passing an admixture of argon and carbon disulfide vapor over the heated sample contained in a carbon reaction chamber. Argon was used as a

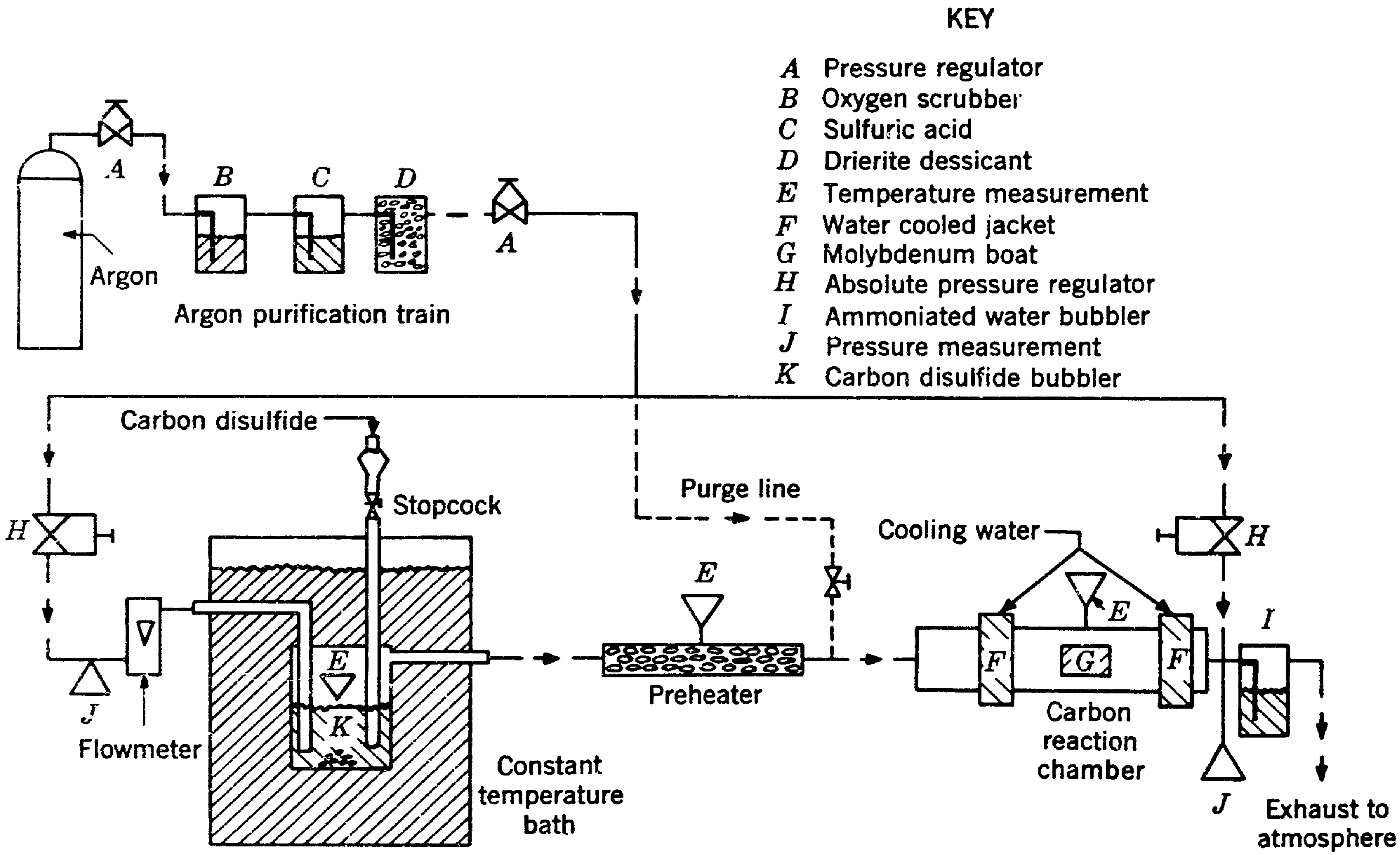


Figure 1. Schematic Flow Diagram of the Experimental Apparatus.

TABLE III

QUALITATIVE SPECTROCHEMICAL ANALYSIS FOR CERIA

Major Constituent - Cerium

Minor Constituents	%			%
Y	.01	Fe		.001
Yb	.005	Mg		.001
Pr	.01	Mn	less than	.001
Dy	.01	Al	less than	.001
La	.005	Cu	less than	.0005
Sm	.001	Ca	less than	.005
Si	.001	Cr	less than	.001

Total Impurities are Less than 400 ppm.

Elements not Detected

Ba	P	Be	Zr
Cd	Pb	Mo	Ni
As	Sn	V	Co
Sb	W	Ag	Gd
Te	Ge	Zn	Nd
B	Bi	Ti	

TABLE IV

INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR HIGH PURITY CERIA FROM WHICH SULFIDES WERE SYNTHESIZED (Cr-RADIATION)

d Spacing (A)	Relative Intensity (I/I_0)	hkl (I)	hkl (II)
4.65	3		(211)
4.03	1		(220)
3.44	2		(311)
3.12	100	(111)	
2.84	1		(400)
2.71	25	(200)	
2.42	1		(332)
2.10	1		(520, 432)
1.957	1		(530, 433)
1.913	53	(220)	
1.790	2		(621, 540, 443)
1.632	36	(311)	
1.563	8	(222)	

Structure	a_o (A)	Compound
I FCC	5.41	CeO_2
II Cubic	11.39	Ce_2O_3

carrier gas. Traces of oxygen and water vapor contaminants were removed from the argon gas stream, prior to use in the system, by passing the gas stream through an oxygen absorber column followed by a dessicant train. The oxygen scrubber was a preparation of 20 grams of potassium hydroxide dissolved in 100 ml of water to which was added 2 grams of anthrquinone beta sulfonate and 15 grams of sodium hydrosulfite. The dessicant train contained two drying agents, sulfuric acid and anhydrous calcium sulfate crystals coated with a cobalt chloride indicator. The relatively dry (estimated dew point minus 45°F) oxygen-free argon gas was then metered under constant pressure at a flow rate of 0.8 standard cubic feet per hour through a constant temperature liquid carbon disulfide (CS_2) tower. The temperature of the liquid carbon disulfide throughout the test was held at 42 ± 0.5°C by means of a constant temperature water bath. As a further precaution against the entry of moisture into the system, 30 grams of phosphorous pentoxide was added to the liquid carbon disulfide column. After depletion, additional carbon disulfide was added to the chamber through a separatory funnel with an integral stop-cock. During the replenishing operation, care was taken to exclude air from the system. Before passing the ensuing admixture of carbon disulfide and argon gas into the carbon reaction chamber containing the heated sample of ceria (CeO_2), the gas stream was preheated to approximately 220°C in a combustion tube furnace packed with molybdenum chips. The spent vapor from the reaction chamber

was ultimately bubbled through a 10 per cent solution of ammonium hydroxide and exhausted to the atmosphere. Every effort was made to maintain as closely as possible isopiestic conditions within the carbon reaction chamber during subsequent runs. An estimate of the magnitude of the pressure variation is five inches of water.

The carbon reaction chamber, a thin-walled carbon combustion tube (3/4 inches I.D. x 40 inches long x 3/16 inch wall thickness), was machined from a solid carbon rod. To retard rapid deterioration and to provide adequate strength, the reaction chamber was encased in a quartz tube. Copper coils were soft soldered to each end of the carbon combustion tube for water cooling. This technique provided a means for restricting the length of the constant temperature zone to approximately three inches. The inlet temperature and pressure of the cooling water were controlled by means of a regulator, because it was found that slight fluctuations in either of these parameters resulted in an appreciable change in the temperature of the hot zone. In fact, this provided a means by which a fine adjustment of the reaction chamber temperature could be obtained by simply regulating the flow of the cooling water through the heat exchangers attached to the end of the carbon tube. The carbon reaction chamber was heated in a Leco Model 2600 combustion tube furnace. Furnace temperature was controlled at the desired level by means of a control potentiometer. The actual temperature of the hot zone in which the sulfurization took place was measured with a Pt/Pt 10 per cent Rh calibrated thermocouple before and after each synthesis run.

After the temperature of the hot zone in the carbon combustion tube had been stabilized, a 25 gram sample of ceria (CeO_2) was placed in a molybdenum boat and inserted into the hot zone. The system was continually purged with argon gas, not only to protect the carbon refractory, but also to minimize oxygen contamination. After the sample was brought up to temperature, carbon disulfide vapor entrained with the carrier gas was passed into the system. This procedure has been previously described. The reaction time for the synthesis was limited to three hours, after which the system was flushed with argon for five minutes before removing the sample from the hot zone. The molybdenum boats now containing the cerium sulfide were quickly cooled under an argon atmosphere at one end of the water cooled combustion tube. The sulfurized sample was screened to minus 150 mesh and then returned to the reaction chamber and the synthesis process was repeated to make certain that complete sample homogeneity had been achieved. After the second sulfurization treatment, the fraction of the sample which passed through 150 mesh screen was stored in argon filled sample bottles.

Thirty-five samples were processed by the above procedure in the carbon combustion tube furnace over the temperature range of 600°C to 1300°C. These samples were prepared at isotherms in 25 degree increments for the purpose of revealing whether the temperature of synthesization might not be a major factor in influencing the sulfurization phenomena attending

a change in crystal structure. It was recognized that if the resultant data were to be effectively evaluated, an estimate of the error attributed to the experimental and analytical methods had to be determined. For this reason, three batches of materials were prepared under similar conditions at each of three different temperature levels. A series of five gram samples were composited from each batch. These representative samples were then submitted in coded lots to two independent consulting laboratories for subsequent wet chemical analyses. The analytical results for sulfur and cerium combined as a sulfide as reported by these laboratories are documented in Tables V and VI. The two laboratories used very similar analytical procedures, which are summarized below. (The analytical methods are detailed in Appendix A.)

Cerium sulfide, when treated with a reducing acid (dilute sulfuric acid), releases sulfur as hydrogen sulfide. Hydrogen sulfide is quantitatively separated by steam distillation and absorbed in a measured excess of ammonical cadmium nitrate solution. After the precipitated cadmium sulfide is removed by filtration, the excess cadmium is determined by titrating the filtrate with the complexing agent, ethylenediaminetetraacetic acid at PH 10, using Eriochrome Black as the indicator. The sulfur combined as a sulfide is computed from the amount of cadmium precipitated.

Cerium combined as a sulfide is selectively determined by using an adaptation of the von Knorre method[17]. This is considered to be a classical

TABLE V

WET CHEMICAL ANALYTICAL RESULTS
REPORTED BY LABORATORY A

Reaction Temperature °C	Combined as Sulfide Ce W%	Combined as Sulfide S W%	S/Ce Molecular Ratio	% Conversion to Sulfide	Residue Ignited and Weighed as CeO_2
597	31.93	13.17	1.803	45.10	53.68
630	57.72	13.49	1.023	71.21	28.41
650	75.60	20.22	1.169	95.82	4.09
* 653	75.45	20.38	1.181	95.83	-----
** 653	75.18	20.85	1.212	96.03	3.18
679	74.95	22.86	1.333	97.81	2.03
700	73.95	24.02	1.420	97.97	2.18
725	74.57	24.79	1.453	99.36	.77
750	75.59	23.20	1.341	98.79	1.12
* 752	75.43	22.76	1.319	98.19	-----
** 752	75.25	22.82	1.326	98.07	1.87
778	76.15	20.67	1.186	96.82	2.96
800	73.60	25.34	1.504	96.94	1.37
825	74.85	23.14	1.352	97.99	1.78
850	74.31	23.92	1.407	98.23	1.63
877	73.73	24.81	1.471	98.54	1.37
900	72.85	26.04	1.562	98.89	1.18
930	72.18	27.58	1.670	99.76	.32
950	74.10	25.42	1.499	99.52	.32
978	73.60	25.85	1.535	99.45	.44
1002	73.25	26.11	1.558	99.36	.53
1022	73.15	26.36	1.575	99.51	.48
1029	73.35	26.54	1.581	99.89	.34
1047	72.68	26.84	1.614	99.52	.42

TABLE V (Continued)

WET CHEMICAL ANALYTICAL RESULTS
REPORTED BY LABORATORY A

Reaction Temperature °C	Combined as Sulfide Ce W%	S W%	S/Ce Molecular Ratio	% Conversion to Sulfide	Residue Ignited and Weighed as CeO_2
* 1050	72.95	26.91	1.612	99.86	-----
** 1050	72.75	27.10	1.628	99.85	.23
1090	72.18	27.34	1.656	99.52	.42
1115	71.29	27.20	1.667	98.49	1.37
1140	71.65	26.33	1.606	97.98	2.19
1200	72.16	25.40	1.539	97.56	2.31
1250	72.35	25.15	1.519	97.50	2.34
1300	72.44	24.91	1.503	97.35	2.48

*Second batch prepared under the same conditions as the first batch.

**Third batch prepared under the same conditions as the first batch.

TABLE VI

WET CHEMICAL ANALYTICAL RESULTS
REPORTED BY LABORATORY B

Reaction Temperature °C	Combined as Sulfide Ce W%	Combined as Sulfide S W%	S/Ce Molecular Ratio	% Conversion to Sulfide
650	75.72	20.35	1.175	96.07
* 653	75.59	20.82	1.204	96.41
** 653	75.52	20.65	1.195	96.17
750	75.44	23.15	1.341	98.59
* 752	75.59	22.92	1.325	98.51
** 752	75.31	23.15	1.344	98.46
800	75.55	21.35	1.235	96.90
941	71.60	27.81	1.698	99.41
960	73.92	25.28	1.495	99.20
1047	72.85	26.73	1.604	99.58
* 1050	73.05	26.85	1.607	99.90
** 1050	72.95	26.78	1.605	99.73
1278	72.38	25.01	1.510	97.39

*Second batch prepared under the same conditions as the first batch.

**Third batch prepared under the same conditions as the first batch.

volumetric method in which cerium is quantitatively oxidized from the +3 to the +4 state by ammonium persulfate in the presence of silver ions. The ceric ion is subsequently reduced to the +4 state by titration with standard ferrous sulfate solution. Since cerium oxide is insoluble in dilute sulfuric acid, the remaining residue was ignited and weighed as Ceria (CeO_2). These results are shown in Table V.

An X-ray diffraction examination of each sample was made immediately after the synthesis run. The material was mounted in a plastic sample holder with no additional crushing and screening. This treatment was used to keep the sulfur losses at a minimum. Powder patterns were recorded on an X-ray diffraction trace obtained from a G. E. XRD-5 X-ray Diffractometer. Filtered chromium radiation was used rather than copper radiation because of the relatively large number of closely spaced lines at low Bragg angles. Also, the selection of a target material with a lower atomic number served a dual purpose in that the amount of fluorescent scattering was considerable reduced. The X-ray diffraction traces are summarized graphically in Figures 2 through 6 inclusive.

The apparent densities of the compacted samples formed over the temperature range of 600°C to 1300°C were determined by the following procedure. Powdered ceric oxide (CeO_2) was cold pressed under 40 tons/square inch pressure in a double acting compacting die which had a rectangular cross section 1/2 inch x 1-1/2 inches. The raw compacts were placed in

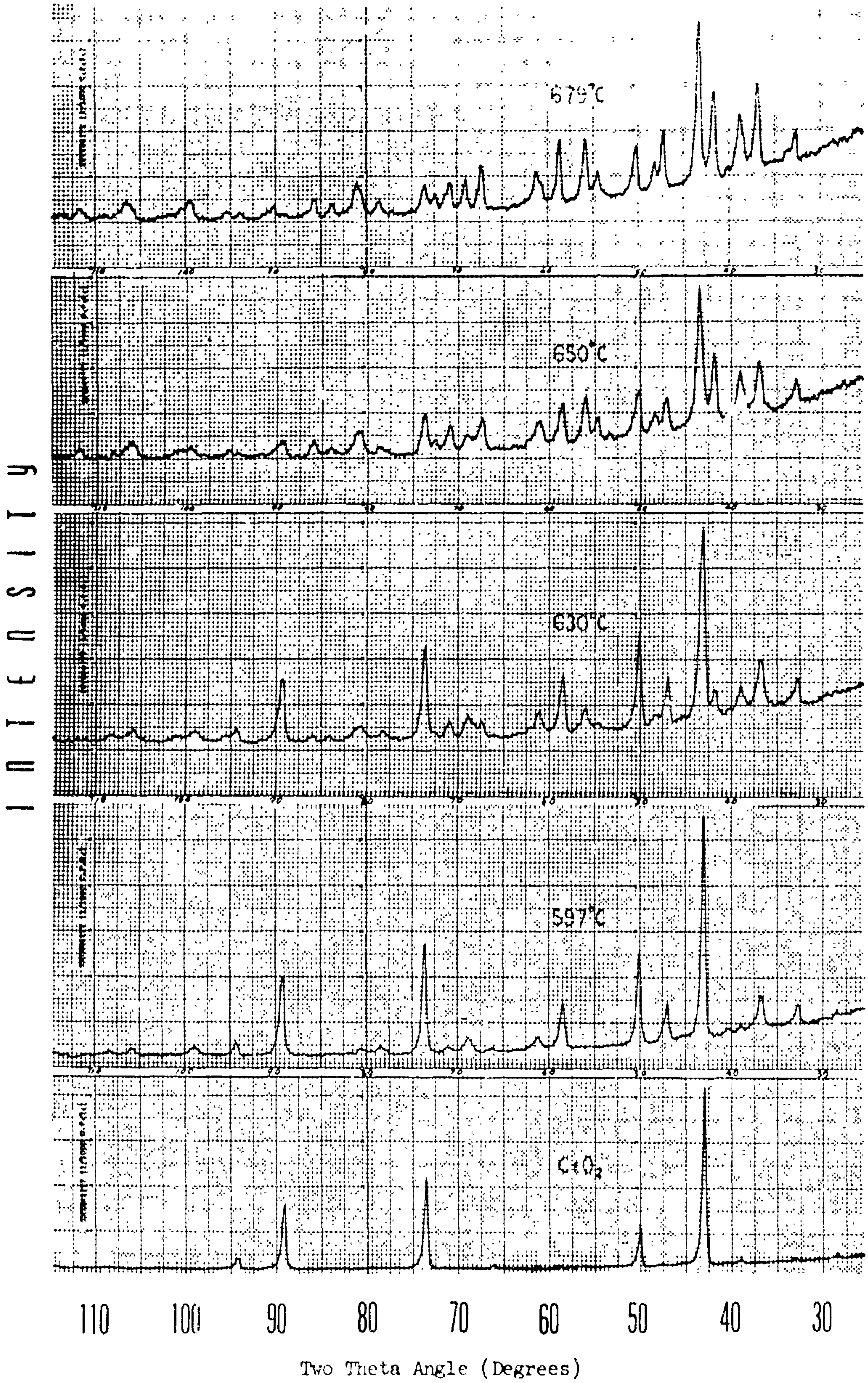


Fig. 2. Comparative X-Ray Diffraction Traces of Cerium-Sulfur Compounds Synthesized in CS_2 Atmosphere at Temperature Noted Above Each Curve.

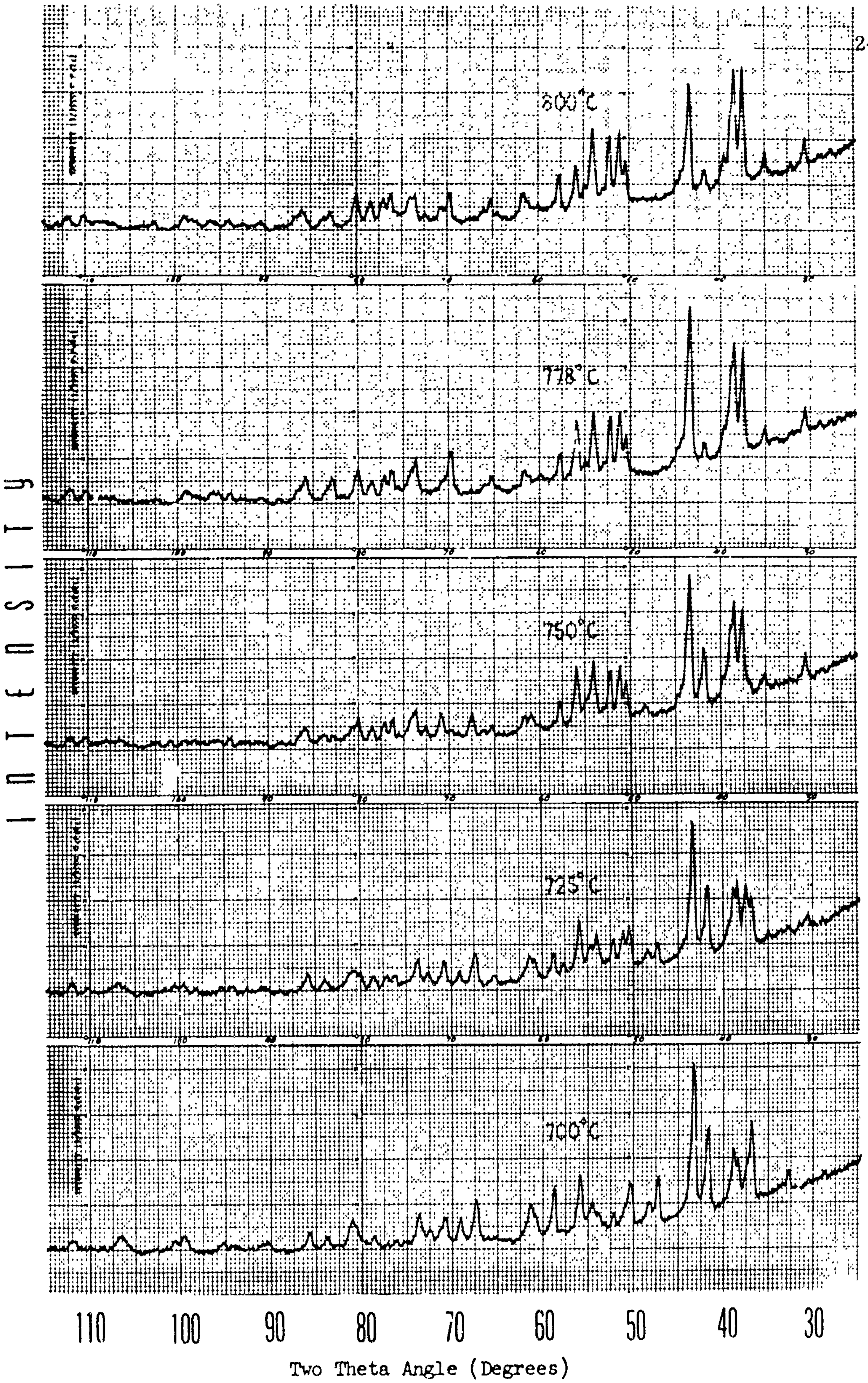


Fig. 3. Comparative X-Ray Diffraction Traces of Cerium-Sulfur Compounds Synthesized in CS_2 Atmosphere at Temperature Noted Above Each Curve.

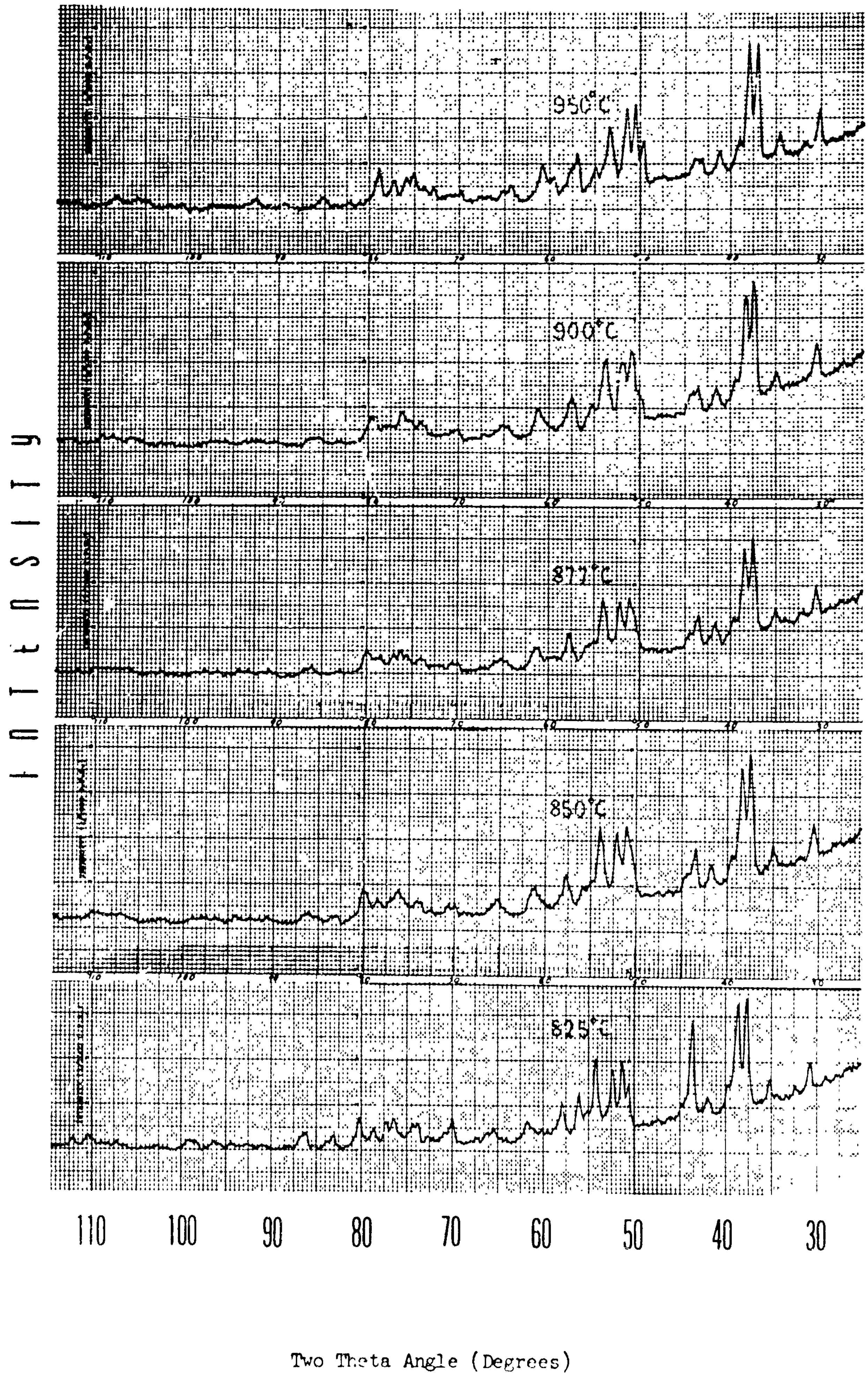


Fig. 1. Comparative X-Ray Diffraction Traces of Cerium-Sulfur Compounds Synthesized in CS_2 Atmosphere at Temperature Noted Above Each Curve.

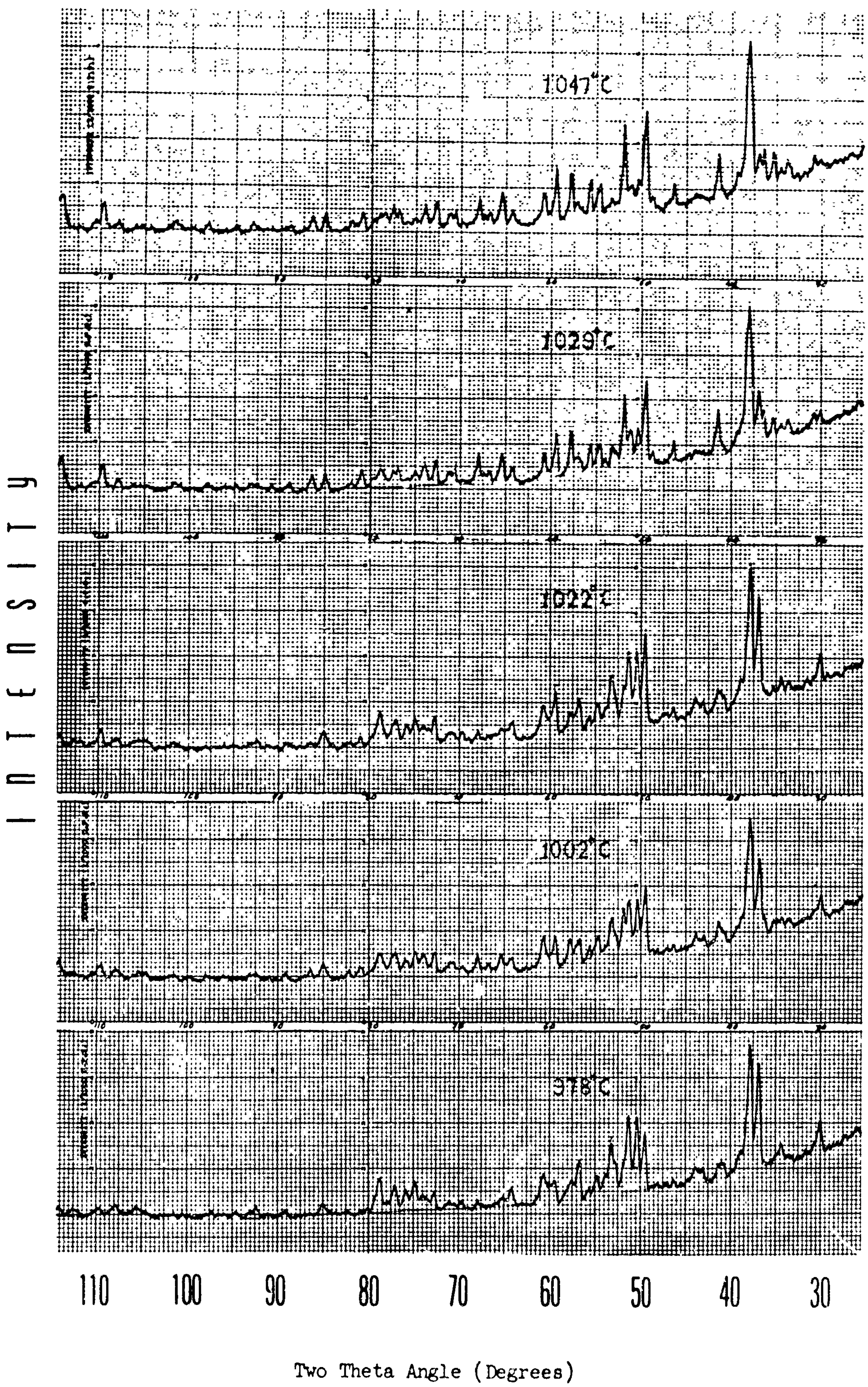
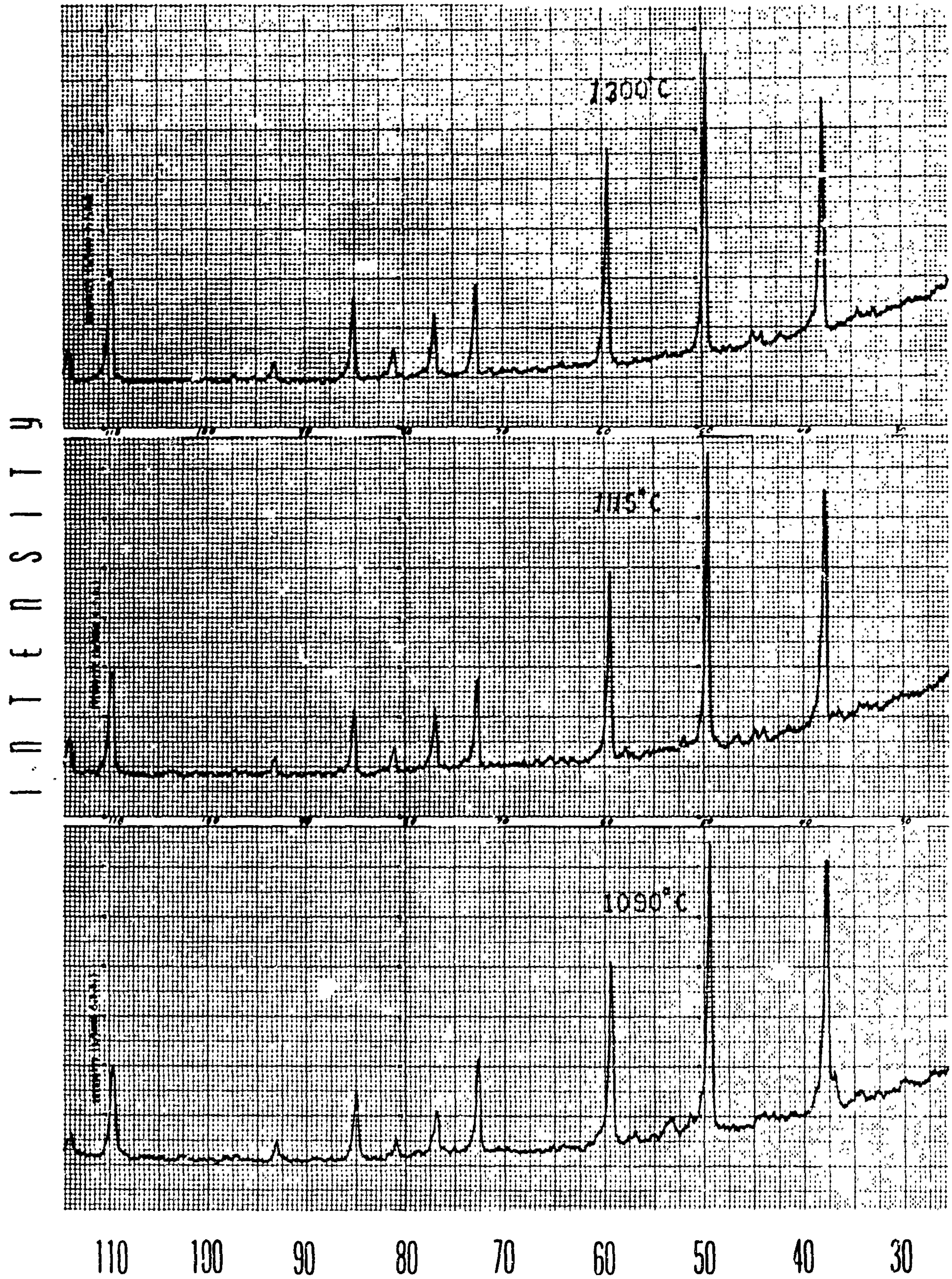


Fig. 5. Comparative X-Ray Diffraction Traces of Cerium-Sulfur Compounds Synthesized in CS_2 Atmosphere at Temperature Noted Above Each Curve.



Two Theta Angle (Degrees)

Fig. 6. Comparative X-Ray Diffraction Traces of Cerium-Sulfur Compounds Synthesized in CS_2 Atmosphere at Temperature Noted Above Each Curve.

a molybdenum boat and sintered for six hours at temperature in the carbon reaction chambers under the same conditions as previously described for the preparation of sulfides. After sintering, the compact was rapidly cooled to room temperature and subsequently the density of the sintered compact was determined by direct measurement and weighing. The results are shown graphically in Figure 7. Some of the physical properties of the synthesized cerium sulfide compounds are shown in Table VII.

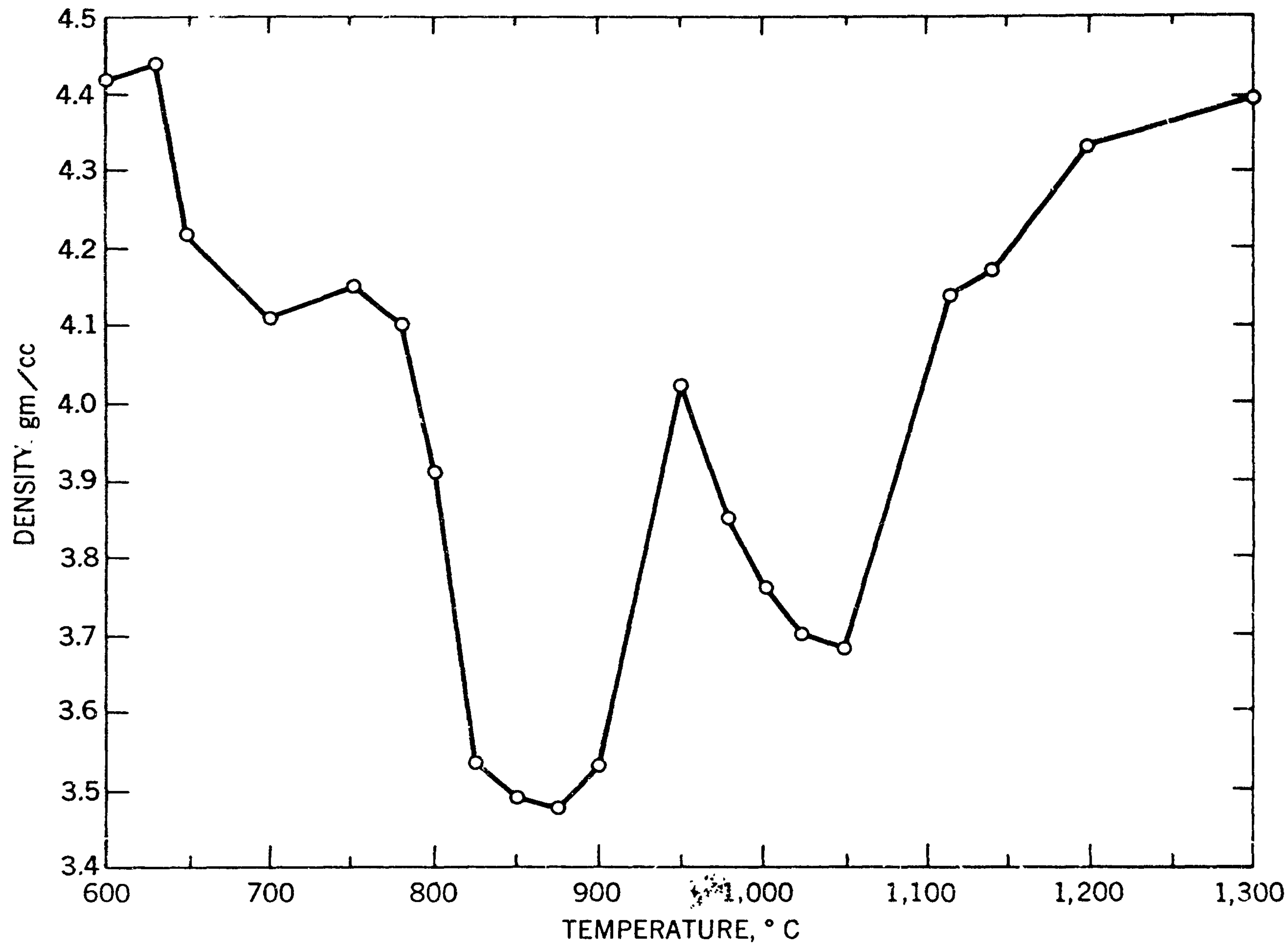


Figure 7. Effect of Synthesis Temperature on the Density of the Cerium Sulfide Compounds Prepared from Compacted Ceric Oxide Samples.

TABLE VII

PHYSICAL PROPERTIES OF CERIUM SULFIDE COMPOUNDS

Temperature °C	Apparent Density Gms/cc	Color of Compound
597	4.42	Gray with brownish tint
630	4.44	Slate gray with slight brownish tint
650	4.42	Slate gray (bluish cast)
679		Slate gray (bluish cast)
700	4.11	Slate gray (bluish cast)
725		Slate gray with reddish tint
750	4.15	Dark gray with slight maroon tint
778	4.10	Dark gray with a definite maroon tint
800	3.91	Light maroon with grayish cast
825	3.53	Light maroon
850	3.46	Maroon
877	3.42	Dark maroon
900	3.48	Maroon with reddish tint
950	4.02	Red-maroon
978	3.85	Not quite as much maroon as 950°C sample
1002	3.76	Dark maroon with a reddish cast
1022	3.70	Dark maroon with a reddish cast
1029		Dark gray with definite maroon tint
1047	3.82	Not quite as dark as 1029°C sample
1115	4.14	Light maroon
1140	4.17	Dark gray with a definite maroon tint
1200	4.33	Light gray with a slight maroon cast
1300	4.36	Light gray with a maroon cast

IV DISCUSSION OF EXPERIMENTAL RESULTS

The results from the data collected in this investigation are discussed in the following sequence; preparation of cerium sulfide compounds, wet chemical analytical results and the X-ray diffraction studies.

A. Preparation of Cerium Sulfide Compounds

The use of the carbon combustion tube furnace shown in Figure 1 is unique for the preparation of cerium sulfide compounds. The system was developed for this investigation in 1960 and has proven itself to be very effective in providing close control of the temperature and flow parameters. This has now been established from the exceptionally good reproducibility of the chemical analyses data compiled in Tables V and VI. It can therefore be concluded from the consistency of the results for the cerium sulfide compounds synthesized at the different isotherms, that the initial objective of this investigation (i.e. producing cerium sulfide compounds for an isothermal study) has been successfully accomplished.

The usual method for preparing cerium sulfide compounds as reported in the literature was a modification of the system described by Eastman et al.[1]. Their design incorporated a reaction chamber consisting of a sealed graphite crucible containing the ceric oxide, into which hydrogen sulfide gas was injected and allowed to permeate throughout the sample

and finally exhaust through the pores of the graphite wall. The unit was heated by an induction coil and temperature measurements were made with an optical pyrometer. While their system does minimize oxygen contamination, it was decided that for an isothermal study, a more sophisticated method would be desirable. The wisdom of this decision is obvious when one compares the merits of both systems. Some of the more important advantages of the carbon combustion tube method are listed below.

(A) The gas flow is more uniform throughout the combustion chamber. Excess sulfur build up, due to plugged pores, is eliminated completely.

(B) The simplified temperature control makes it possible to reproduce the chemical results.

(C) It is more readily adapted to a continuous process because the reaction chamber is not cooled down after each batch is produced. Since there are no critical mating surfaces to deteriorate from chemical attack, the frequent machining of these surfaces is eliminated. In fact, after 300 hours of continuous operation, an examination of the carbon combustion tube showed that it was still in good condition.

It has been previously pointed out that Carter[13] had suggested the possibility of using carbon disulfide as the chalcogenide gas. However, there was nothing available in the literature concerning this particular application. Therefore, it was found necessary to experimentally design the

system so that the interaction of other parameters; namely, gas flow, mixing, heat and mass transfer produced optimum conditions. While taking these factors into consideration, a reasonable period of time had to be provided for the sulfide reaction to take place.

To establish the length of time required to approach equilibrium conditions, sulfide samples were prepared at a given temperature for different time intervals. The rate of argon and carbon disulfide gas flow was then compromised with the length of time at temperature to obtain a sample which, by means of X-ray diffraction patterns, appeared to be uniform throughout in composition. For example, after two hours at 900°C, an X-ray diffraction examination of the cerium sulfide compound indicated that the sample was homogeneous. Even though the gas flow was maintained at a minimum to prevent deposition of carbon, an excess of sulfur was always present.

During the course of this investigation every precaution and care was exercised to avoid introducing experimental error either in technique or measurements. The time consumed in producing just one sample was in the order of ten hours, excluding the number of initial runs which failed because of inexperience in handling these materials.

B. Wet Chemical Analytical Results

As a result of the chemical studies of the cerium-sulfur system, sufficient data has been obtained at isotherms ranging from 600°C to 1300°C

to construct a partial binary diagram. The diagram is shown graphically in Figure 8. A thorough search of the literature has failed to disclose the existance of any diagram or chemical data to substantiate these results. Evidently, an isothermal diagram of the cerium-sulfur system for the 600°C to 1300°C temperature region has not been published to date.

From Figure 8 it can be seen that there are five different slopes to the sulfurization curve within the temperature span of 700°C. The wet chemistry results for these different temperature regions are summarized in Table VIII.

J. Flahaut and M. Guittard[2] have reported the following compositions for the cerium sesquisulfides.

Alpha phase	25.56 W per cent S	73.82 W per cent Ce
Beta phase	25.71 W per cent S	74.45 W per cent Ce

Eastman et al.[1] has indicated that the gamma phase of cerium sesquisulfide contains 25.5 weight per cent sulfur if the starting oxide is pure and as high as 26.2 weight per cent sulfur if the starting material is the commercial grade oxide.

From an analysis of variance for the replicated data shown in Tables V and VII it was concluded that on the 95 per cent confidence level there is no significant statistical difference between the samples synthesized at the same temperatures; there is no significant difference in chemical results reported by the two independent laboratories and the precision of the analysis for sulfur and cerium is approximately ± 0.1 per cent.

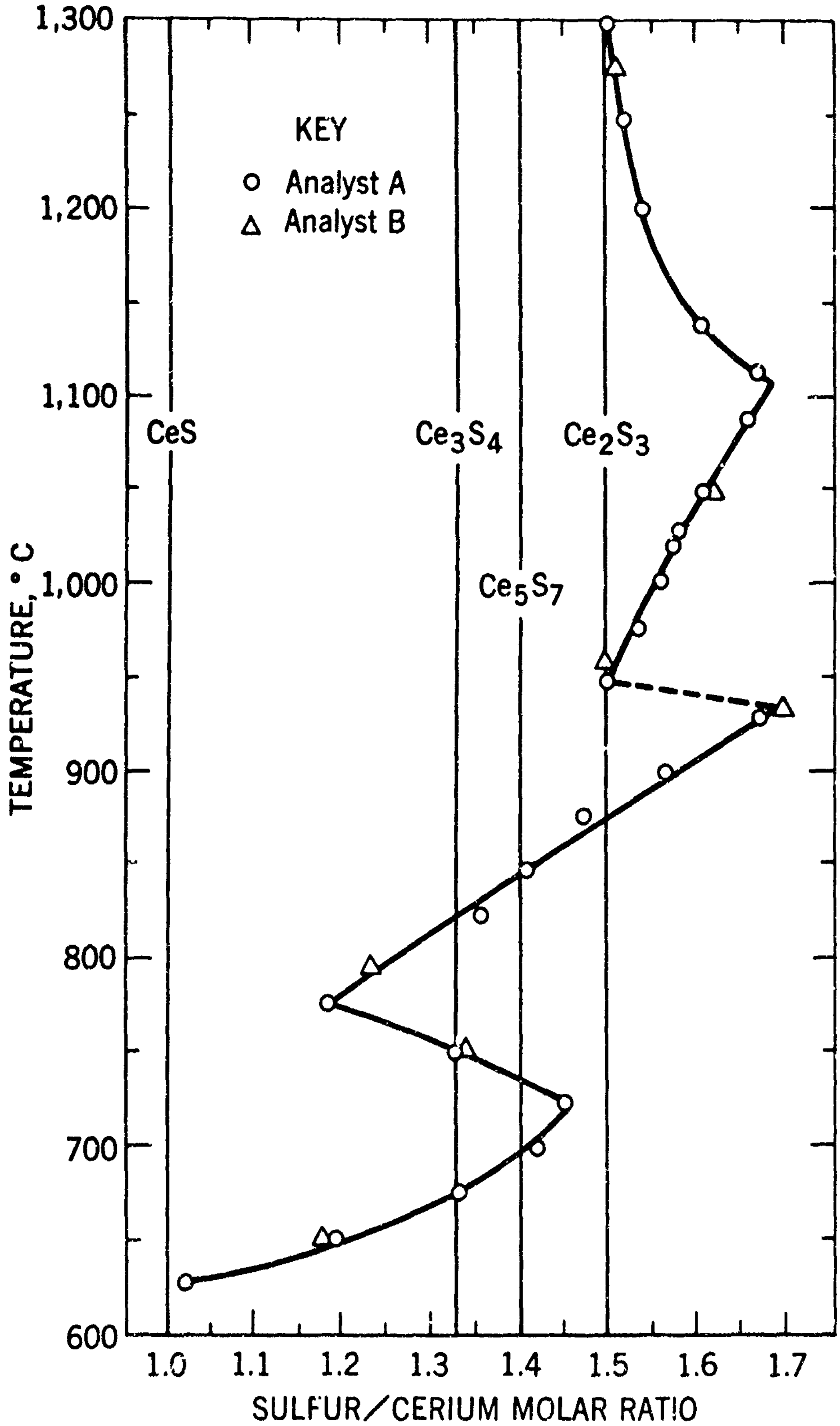


Figure 8. Sulfurization Curve for the Cerium Sulfide Compounds Shown as a Function of the Synthesis Temperature.

TABLE VIII

SUMMARY OF THE WET CHEMICAL RESULTS

Region	Temperature Range	Per Cent S	Per Cent Ce	Molar Ratio S/Ce	Per Cent Conversion to Sulfide
1	625-725°C	13.5-24.8	57.7-74.6	1.02-1.45	71.2-99.4
2	725-775°C	24.8-20.7	74.6-76.2	1.45-1.19	99.4-9[illegible]
3	775-950°C	20.7-25.4	76.2-74.1	1.19-1.50	96.9-99.5
4	950-1100°C	25.4-27.2	74.1-71.3	1.50-1.67	99.5-98.5
5	1100-1300°C	27.2-24.9	71.3-72.4	1.67-1.50	98.5-97.3

C. X-Ray Diffraction Results

The relationship between the X-ray diffraction spectra and reaction temperatures for the cerium sulfide compounds prepared in this investigation is shown graphically in Figures 2 to 6 inclusive. Because of the complex nature of the X-ray diffraction traces below 1100°C, the patterns are very difficult to index. There is no single phase compound listed in the literature which can account for all of the lines appearing on the traces. This is indicative that either there is more than one phase present or the cerium sulfide compounds have different structures than the ones which are normally accepted in the literature.

In the temperature region from 950°C to 1100°C, there is evidence that a mixture of several phases is present. Two of these phases have been indexed as cubic structures. A body-centered cubic phase with an a_0 value of 8.65 A has been identified from the ASTM Index as Ce_3S_4. The second phase is simple cubic with an a_0 value of 8.85 A. However, the indexing for this phase is not listed in the literature. It has been established from this investigation that the body-centered cubic gamma phase of Ce_2S_3 exists above 1100°C. Eastman et al.[6] has pointed out that the presence of a small amount of oxygen in solid solution in Ce_2S_3 could change its normal Ce_3S_4 (Th_3P_4) type structure to another unknown complex structure, possibly the Th_2S_3 (Sb_2S_3) type crystal structure.

Figure 9 shows the amount of material converted to a sulfide at each temperature level. The maximum yield is obtained in the temperature range of 950°C to 1090°C. This is surprising because it was believed that minute amounts of oxygen contamination were the cause of the complex phase formation. Above 1100°C, the body-centered cubic phase of cerium sesquisulfide is the only structure present, but there is a relatively constant quantity of ceria present (2 per cent). Only trace amounts of carbon and molybdenum have been detected in any of the samples.

The d values and the relative intensity of the lines shown on the X-ray diffraction patterns are compiled in Appendix B. After conventional graphical methods were unsuccessful in indexing the complex X-ray spectra, a computer program was written using the reciprocal lattice technique proposed by Ito[18]. The computer program has correctly indexed the reduced cell of $MgWO_4$ as monoclinic. Since the structure of this material was already known, it served as a good example for debugging the computer program.

However, the computer program has failed to completely index any of the complex patterns resulting from this investigation. The structure of the sulfide compounds prepared below 950°C was indexed as monoclinic with the following lattice parameters:

a_o = 1.42 A

b_o = 6.19 A

c_o = 7.16

beta = 99.98°

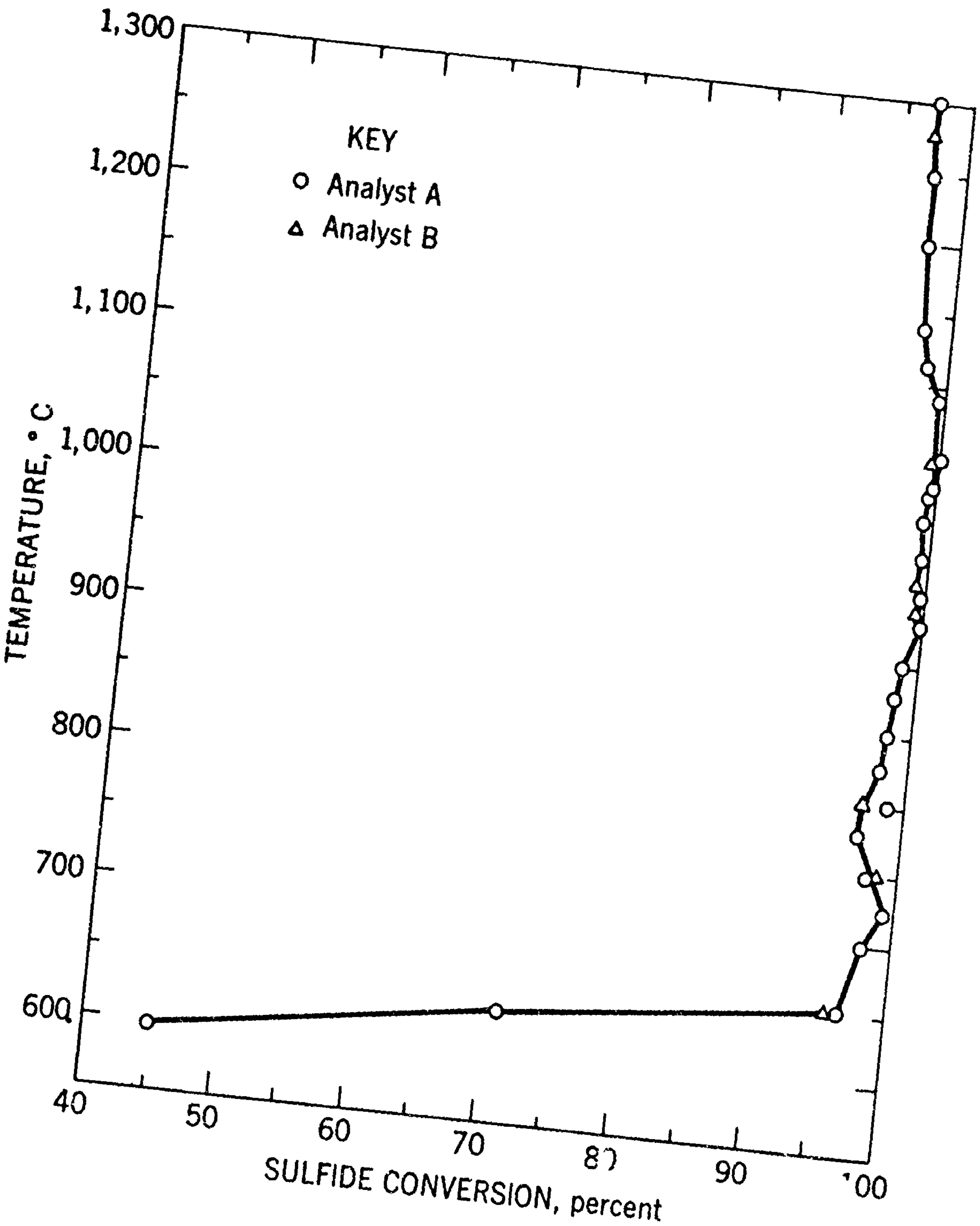


Figure 9. The Amount of Ceric Oxide Converted to Sulfide Shown as a Function of the Synthesis Temperature.

Unfortunately, some of the lines appearing on the X-ray patterns could not be indexed with this structure. The only structure for the compounds prepared below 950°C in which all the lines could be indexed was in the orthorhombic system having the lattice parameters

$$a_0 = 12.41 \text{ A}$$

$$b_0 = 10.84 \text{ A}$$

$$c_0 = 8.74 \text{ A}.$$

The validity of the indexing of a system with extremely large lattice parameters is seriously questioned. Possibly, the difficulty can be attributed to the absence of certain reflections from the X-ray spectra. It was recognized that the absence of certain reflections would be troublesome with any indexing procedure, but facilities and time were not available for growing a single crystal.

D. Density Measurements of Sintered Compacts

Figure 7 shows a graphical tabulation of the apparent density measurements for the quenched sintered compacts. Some difficulty was experienced in obtaining flat specimens that were completely free from warping which occurred during sintering. The trend in the density curve follows closely the changes in slopes observed on the sulfurization curve shown in Figure 8. The density of the compacts decreases to minimum value of 3.5 gm/cc at 900°C. It is in this region that the most complex sulfide phase exists. From 1100°C to 1300°C, the density gradually increases from 4.1 to 4.1 gm/cc. This corresponds to the body-centered cubic Ce_2S_3 phase region on

the sulfurization curve. From 950°C to 1100°C, there is another significant change in the density curve which also can be followed on the sulfurization curve.

V SUMMARY AND CONCLUSIONS

The cerium-sulfur system has been investigated isothermally over the temperature range of 600°C to 1300°C in approximately 25 degree increments. A method for the preparation of the sulfide compounds from ceria has been developed and the chemistry of the process is shown in both graphical and tabular form. From this investigation, a graphical tabulation of the complex X-ray diffraction spectrograms for the various reaction products produced at the different isotherms is now available.

As a result of this study and research, the following conclusions may be drawn.

(A) Cerium sulfide compounds can be synthesized from ceric oxide by the carbon disulfide method developed in this investigation. A series of 26 cerium sulfur compounds were prepared over the temperature range of 600°C to 1300°C. A second series of cerium sulfide compounds were made in this temperature range to duplicate the first batch of samples. The experimental results obtained from these two series of samples are in very close agreement, as shown in Tables V and VI.

(B) X-ray diffraction patterns for these cerium sulfide compounds are compared graphically in Figures 2 to 6. The d values and relative intensity measurements are tabulated in Appendix B.

(C) Complex X-ray diffraction spectra were obtained for the compounds synthesized below 950 C. Unfortunately, because

of the many lines appearing on the diffraction traces, it was impossible to index these patterns by conventional methods. Even though these patterns are reproducible at the different isotherms, it is now apparent that the true lattice constants cannot be determined until single crystals become available for study.

(D) From 950°C to 1100°C, there is evidence that a mixture of several phases is present. Two of these phases have been indexed as cubic structures. A body-centered cubic Ce_3S_4 type structure with an a_o value of 8.65 A is predominant. The second phase is simple cubic, with an a_o value of 8.85 A. However, the indexing for this material is not listed in the literature.

(E) The body-centered cubic gamma Ce_2S_3 phase exists above 1100°C.

(F) Sufficient chemical analysis data has been submitted for the construction of a diagram of the cerium-sulfur system shown in Figure 8. The results of the chemical analysis can be reproduced within one per cent of the constituent present.

(G) Above 650°C more than 95 per cent of the ceria was converted to a sulfide as shown in Figure 9. A surprising phenomena

exists in the temperature region above 1100°C in that progressively less material is converted to the sulfide with an increase in the reaction temperature. It is in this region that the gamma phase of Ce_2S_3 exists.

(F) In the low temperature region, where the most complex phase is formed, the sintered compacts have the lowest density as shown in Figure 7.

APPENDIX A

APPENDIX A

Analytical Method for Determination of Sulfur and Cerium Combined as a Sulfide

I. Apparatus

Distillation Apparatus (Micro, Improved Kennerer-Hallett Type, Fisher Scientific Company No. 21-150)

Flask (Digestion-Distillation, Fisher Scientific Company No. 21-151)

Fisher All-Temperature Heater (Type A, Fisher Scientific Company No. 11-426)

II. Reagents

Sulfuric Acid (10 $^{v}/_{o}$)

Ammonical Cadmium Nitrate (0.15M) Solution

Dissolve 46.274 gms. of reagent grade cadmium nitrate (CD $(NO_3)_2 \cdot 4H_2O$) in 20 ml. of deionized water to which 300 ml. of concentrated ammonium hydroxide had been added. Dilute to one liter with deionized water.

Ethylenediaminetetraacetic Acid (0.10M) - Complexing Agent

Dissolve 37.22 gms. of reagent grade disodium ethylenediaminetetraacetic acid dihydrate and dilute to one liter with deionized water. The EDTA solution is standardized with a known amount of high purity cadmium metal.

Eriochrome Black T Indicator (0.2 per cent alcoholic solution)

Dissolve 0.200 gms. of Eriochrome Black T Indicator in 100 ml. methanol alcohol.

Ferrous Sulfate Solution (0.05M)

Dissolve 11.1999 gms. of ferrous sulfate in 500 ml. of deionized water containing 10 ml. sulfuric acid and dilute to one liter with deionized water. Standardize solution with primary standard potassium dichromate on the same day it is to be used.

Ferrion Indicator

Dissolve 2.34279 gms. of phenanthroline and 1.3901 gms. of $Fe_2SO_4 \cdot 7H_2O$ in 200 ml. of deionized water.

PH 10 Buffer

Dissolve 67.5 gms. of ammonium chloride in 570 ml. concentrated ammonium hydroxide and dilute to one liter with deionized water.

III. Procedure for Sulfur Determination

Weigh a 1.5000 to 2.000 gms. of sample into a clean dry digestion-distillation flask. Pipet 20 ml. of ammonical cadmium nitrate solution into receiver flask and submerge under condenser tip. Attach digestion-distillation flask to apparatus and add 10 ml. of dilute sulfuric acid (1:10) and steam distill for 15 minutes. Remove distillation flask and rinse condenser with deionized water. Filter precipitated cadmium sulfide into medium porosity sintered glass filter crucible. Wash thoroughly with dilute ammonium hydroxide (1:20). To the filtrate add five drops of Eriochrome Black T Indicator and titrate to pure blue end point with 0.1 M EDTA.

$$\text{per cent S} = \frac{((Mcd\ Vcd) - (MeVe))\ (.03207)\ (100)}{\text{sample weight}}$$

Mcd = molarity of ammonical cadmium solution

Vcd = volume of ammonical cadmium solution

Me = molarity of EDTA

Ve = volume of EDTA

IV. Determination of Cerium

Filter the contents of the digestion-distillation flask through a Whatman No. 40 filter paper and wash thoroughly with dilute sulfuric acid (1:20).

Add 5 ml. of concentrated nitric acid, 5 ml. of silver nitrate solution (2.5 gms. $AgNo_3/L$), and 5 gms. of ammonium persulfate ($(NH_4)_2S_2O_8$) to the filtrate and boil the solution for 15 minutes to destroy excess ammonium persulfate. After cooling to room temperature, add 5 drops of Ferroin indicator and titrate to reddish-orange end point with 0.05 M ferrous sulfate.

$$\text{per cent Ce} = \frac{(VfNf)\ (.14013)\ (100)}{\text{sample weight}}$$

Nf = normality of ferrous solution

Vf = volume of ferrous solution

APPENDIX B

INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 597°C (Cr-RADIATION)

d Spacing (A)	Relative Intensity (I/I_0)	hkl (I)	hkl (II)
4.65	2	(111)	
4.05	8	(200)	
3.63	16	(210)	
3.32	2	(211)	
3.12	100	(300)	(111)
2.87	16	(220)	
2.71	40		(200)
2.34	20	(222)	
2.25	6	(320)	
2.02	6	(400)	
1.971	2	(410, 322)	
1.911	52	(411, 330)	(220)
1.811	2	(420)	
1.772	2	(421)	
1.630	25		(311)
1.560	6		(222)

Structure	a_o (A)
I Simple Cubic	8.11
II FCC	5.41

INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 630°C (Cr-RADIATION)

d Spacing (A)	Relative Intensity (I/I_0)	hkl (I)	hkl (II)
6.25	5		
4.05	15	(200)	
3.63	25	(210)	
3.43	12		
3.21	12		
3.12	100		(111)
2.87	25	(220)	
2.79	3		
2.71	52	(300)	(200)
2.44	12	(311)	
2.34	27	(222)	
2.26	10	(320)	
2.06	10		
2.02	12	(400)	
1.971	8	(410, 322)	
1.911	50	(411, 330)	(220)
1.813	5	(420)	
1.772	8	(421)	
1.629	35		(311)
1.560	8		(222)

Structure	a_0 (A)
I Simple Cubic	8.10
II FCC	5.41

INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 650°C (Cr-RADIATION)

d Spacing	Relative Intensity (I/I_0)	hkl
6.22	6	(200)
4.04	20	(012)
3.62	33	(030)
3.47	20	(130)
3.43	30	(022)
3.21	47	(131)
3.09	100	(400)
2.87	23	(103)
2.79	13	(032)
2.69	33	(420)
2.49	16	(240)
2.44	30	(412)
2.34	30	(511)
2.26	17	(142)
2.06	23	(204)
2.02	9	(214)
1.971	17	(423)
1.936	6	(304)
1.909	23	(152)
1.809	3	(060)
1.763	17	(622)
1.711	3	(115)
1.679	13	(205)

INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 679°C (Cr-RADIATION)

d Spacing (A)	Relative Intensity (I/I_0)	hkl
6.22	9	(200)
4.07	20	(012)
3.62	51	(030)
3.47	23	(130)
3.45	34	(022)
3.22	51	(131)
3.10	100	(400)
2.80	17	(032)
2.70	31	(420)
2.50	17	(240)
2.47	37	(500)
2.44	37	(412)
2.34	37	(511)
2.26	11	(142)
2.25	20	(133)
2.07	26	(204)
2.02	20	(214)
1.976	20	(423)
1.936	9	(304)
1.911	17	(152)
1.837	3	(612)
1.807	9	(060)
1.772	17	(523)
1.763	20	(622)
1.714	6	(115)
1.682	11	(205)

INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 700°C (Cr-RADIATION)

d Spacing (A)	Relative Intensity (I/I_0)	hkl
6.25	6	(200)
4.07	15	(012)
3.62	55	(030)
3.56	27	(102)
3.48	30	(130)
3.44	36	(022)
3.22	55	(131)
3.10	100	(400)
2.86	30	(103)
2.80	12	(032)
2.69	30	(420)
2.66	12	(104)
2.60	9	(331)
2.53	12	(402)
2.50	18	(240)
2.48	12	(500)
2.44	39	(412)
2.38	3	(223)
2.34	33	(511)
2.26	15	(142)
2.25	24	(133)
2.06	27	(204)
2.02	15	(214)
1.976	18	(423)
1.936	9	(304)

(Continued)

INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 700°C (Cr-RADIATION)

d Spacing (A)	Relative Intensity (I/I_0)	hkl
1.911	21	(152)
1.858	6	(252)
1.834	6	(612)
1.807	9	(060)
1.781	3	(523)
1.763	21	(622)
1.716	9	(115)
1.685	12	(205)

INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 725°C (Cr-RADIATION)

d Spacing	Relative Intensity (I/I_0)	hkl
6.22	7	(200)
4.35	9	(002)
4.22	3	(300)
4.05	7	(012)
3.81	7	(112)
3.62	34	(030)
3.56	45	(102)
3.47	48	(130)
3.44	45	(022)
3.39	14	(212)
3.22	52	(131)
3.10	100	(400)
3.08	2	(321)
2.85	14	(103)
2.79	10	(032)
2.68	28	(420)
2.66	28	(104)
2.60	21	(331)
2.52	24	(402)
2.49	17	(240)
2.48	14	(500)
2.44	38	(412)
2.38	10	(223)
2.33	17	(511)
2.32	7	(313)
2.26	14	(142)

(Continued)

INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 725°C (Cr-RADIATION)

d Spacing (A)	Relative Intensity (I/I_0)	hkl
2.24	17	(133)
2.12	7	(403)
2.06	24	(204)
2.02	10	(214)
1.976	20	(423)
1.936	10	(304)
1.911	20	(152)
1.855	10	(252)
1.839	10	(612)
1.807	10	(060)
1.781	14	(523)
1.768	14	(622)
1.711	10	(115)
1.690	14	(205)

INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 750°C (Cr-RADIATION)

d Spacing (A)	Relative Intensity (I/I_0)	hkl
4.34	26	(002)
3.81	13	(112)
3.74	13	(301)
3.62	22	(030)
3.56	87	(102)
3.47	96	(130)
3.44	70	(022)
3.38	22	(212)
3.20	52	(131)
3.10	100	(400)
3.03	13	(321)
3.01	8	(302)
2.79	13	(032)
2.74	4	(113)
2.68	35	(420)
2.65	48	(104)
2.60	43	(331)
2.57	13	(421)
2.52	61	(402)
2.50	26	(240)
2.48	22	(500)
2.44	56	(412)
2.37	30	(223)
2.34	13	(511)
2.26	17	(142)
2.24	17	(133)

(Continued)

INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 750°C (Cr-RADIATION)

d Spacing (A)	Relative Intensity (I/I_0)	hkl
2.12	8	(403)
2.10	4	(051)
2.06	22	(204)
2.00	4	(214)
1.976	22	(423)
1.934	13	(304)
1.909	26	(152)
1.902	17	(314)
1.870	8	(034)
1.855	22	(252)
1.839	17	(612)
1.809	13	(060)
1.781	22	(523)
1.770	13	(622)
1.731	8	(701)
1.716	8	(115)
1.680	17	(205)
1.669	8	(443)

INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 778°C (Cr-RADIATION)

d Spacing (A)	Relative Intensity (I/I_0)	hkl
4.34	17	(002)
3.81	17	(112)
3.56	67	(102)
3.47	76	(130)
3.44	23	(022)
3.38	21	(212)
3.21	12	(131)
3.10	100	(400)
2.68	24	(420)
2.65	40	(104)
2.60	36	(331)
2.57	9	(421)
2.52	40	(402)
2.48	12	(500)
2.44	40	(412)
2.37	18	(223)
2.29	3	(422)
2.26	6	(142)
2.24	12	(133)
2.12	12	(403)
2.10	6	(051)
2.07	3	(204)
2.00	27	(214)
1.9[illegible]9	9	(423)
1.936	3	(304)
1.911	24	(152)

(Continued)

INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 778°C (Cr-RADIATION)

d Spacing (A)	Relative Intensity (I/I_0)	hkl
1.900	12	(314)
1.870	3	(513)
1.855	17	(252)
1.839	12	(612)
1.809	9	(060)
1.781	18	(523)
1.731	12	(105)
1.682	18	(205)
1.671	9	(062)

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INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 800°C (Cr-RADIATION)

d Spacing	Relative Intensity (I/I_0)	hkl
7.40	12	(110)
7.47	8	(021)
4.35	24	(002)
4.15	8	(300)
3.81	24	(112)
3.56	100	(102)
3.48	96	(130)
3.39	28	(212)
3.22	20	(131)
3.10	96	(400)
3.05	20	(321)
3.02	12	(302)
2.68	36	(420)
2.65	60	(104)
2.60	60	(331)
2.57	16	(421)
2.52	68	(402)
2.48	24	(500)
2.44	40	(412)
2.37	28	(223)
2.29	8	(422)
2.26	12	(142)
2.24	20	(133)
2.12	20	(403)
2.10	12	(051)
2.00	24	(214)

(Continued)

INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 800°C (Cr-RADIATION)

d Spacing (A)	Relative Intensity (I/I_0)	hkl
1.979	12	(423)
1.936	8	(304)
1.913	24	(152)
1.902	20	(214)
1.858	24	(252)
1.839	24	(612)
1.809	20	(060)
1.781	28	(523)
1.763	8	(622)
1.730	16	(701)
1.718	12	(115)
1.679	20	(205)
1.669	12	(443)

INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 825°C (Cr-RADIATION)

d Spacing (A)	Relative Intensity (I/I_o)	hkl
4.32	23	(002)
4.14	9	(300)
3.79	23	(112)
3.54	64	(102)
3.46	100	(130)
3.37	27	(212)
3.23	14	(131)
3.08	95	(400)
3.02	18	(302)
2.68	41	(420)
2.64	64	(104)
2.59	50	(331)
2.57	9	(421)
2.51	59	(402)
2.48	14	(500)
2.44	36	(412)
2.37	32	(223)
2.29	5	(422)
2.23	18	(133)
2.12	14	(403)
2.10	9	(051)
2.00	27	(214)
1.981	9	(423)
1.934	5	(304)
1.909	18	(152)
1.893	18	(314)

(Continued)
INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 825°C (Cr-RADIATION)

d Spacing (A)	Relative Intensity (I/I_0)	hkl
1.854	23	(252)
1.833	18	(612)
1.807	14	(060)
1.777	32	(523)
1.726	14	(701)
1.713	9	(115)
1.677	18	(205)

INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 850°C (Cr-RADIATION)

d Spacing (A)	Relative Intensity (I/I_o)	hkl
7.36	8	(110)
4.35	27	(002)
4.15	4	(300)
3.81	23	(112)
3.56	100	(100)
3.48	96	(130)
3.39	19	(212)
3.21	19	(131)
3.09	32	(400)
3.02	12	(302)
2.68	42	(420)
2.66	58	(104)
2.61	58	(331)
2.52	64	(402)
2.48	16	(500)
2.44	16	(412)
2.37	27	(223)
2.25	24	(142)
2.12	16	(403)
2.11	12	(051)
1.996	12	(214)
1.981	12	(423)
1.936	4	(304)
1.905	12	(314)
1.858	23	(252)
1.839	19	(612)

(Continued)

INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 850°C (Cr-RADIATION)

d Spacing (A)	Relative Intensity (I/I_0)	hkl
1.809	19	(060)
1.781	27	(523)
1.726	4	(701)
1.679	12	(205)

INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 877°C (Cr-RADIATION)

d Spacing (A)	Relative Intensity (I/I_0)	hkl
7.48	13	(110)
4.34	26	(002)
4.15	4	(300)
3.81	22	(112)
3.69	4	(221)
3.56	96	(100)
3.47	100	(130)
3.38	30	(212)
3.22	22	(131)
3.09	30	(400)
3.03	13	(302)
2.68	30	(420)
2.65	54	(104)
2.60	54	(331)
2.52	54	(402)
2.48	9	(500)
2.37	26	(223)
2.25	18	(142)
2.13	9	(403)
1.996	4	(214)
1.981	4	(423)
1.902	9	(314)
1.866	13	(513)
1.855	22	(152)
1.839	18	(612)

(Continued)

INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 877°C (Cr-RADIATION)

d Spacing (A)	Relative Intensity (I/I_0)	hkl
1.811	18	(060)
1.781	22	(523)
1.677	9	(205)

INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 900°C (Cr-RADIATION)

d Spacing (A)	Relative Intensity (I/I_o)	hkl
7.48	8	(110)
6.46	8	(200)
4.82	4	(120)
4.35	28	(002)
3.82	16	(112)
3.57	100	(100)
3.49	96	(130)
3.40	20	(212)
3.35	8	(031)
3.23	16	(131)
3.09	16	(400)
3.05	16	(302)
2.71	20	(040)
2.67	60	(420)
2.62	48	(331)
2.54	48	(402)
2.47	20	(500)
2.38	28	(223)
2.25	20	(142)
2.15	12	(024)
2.13	12	(403)
2.07	4	(204)
1.996	8	(214)
1.909	8	(152)
1.900	8	(314)
1.876	12	(513)

(Continued)

INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 900°C (Cr-RADIATION)

d Spacing (A)	Relative Intensity (I/I_o)	hkl
1.858	24	(152)
1.792	28	(523)
1.679	20	(205)

INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 950°C (Cr-RADIATION)

d Spacing (A)	Relative Intensity (I/I_o)	hkl (I)	hkl (II)
6.56	8		
4.41	36		(200)
3.86	20		(210)
3.61	100		(211)
3.53	100	(211)	
3.43	28		
3.25	20		
3.11	16		(220)
3.06	16	(220)	
3.03	8		
2.73	36	(310)	
2.68	68		
2.64	64		(311)
2.55	52		(222)
2.52	20		
2.48	20		(320)
2.40	32		
2.38	24		(321)
2.31	16	(321)	
2.26	32		
2.15	12		(410)
2.12	12		
1.998	12		
1.984	4		
1.971	4		(420)

(Continued)

INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 950°C (Cr-RADIATION)

d Spacing (A)	Relative Intensity (I/I_o)	hkl (I)	hkl (II)
1.927	12	(420)	
1.907	4		
1.881	24		(332)
1.862	24		
1.835	20	(332)	
1.802	32		(422)
1.761	4	(422)	
1.693	12	(510, 431)	(511, 333)
1.583	8		

Structure	a_o (A)
I BCC	8.63
II Simple Cube	8.82

INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 978°C (Cr-RADIATION)

d Spacing (A)	Relative Intensity (I/I_o)	hkl (I)	hkl (II)
7.48	7		
5.11	7		(111)
4.42	28		(200)
4.35	11		
4.20	7		
3.87	[illegible]		
3.62	82		(211)
3.53	100	(211)	
3.44	19		
3.27	11		
3.12	11		(220)
3.09	11		
3.06	14	(220)	
2.73	44	(310)	
2.69	57		
2.64	57		(311)
2.62	19		
2.58	22		
2.56	41		(222)
2.53	14		
2.49	19		
2.45	7		(320)
2.41	33		
2.38	14		(321)
2.31	14	(321)	
2.27	26		

(Continued)

INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 978°C (Cr-RADIATION)

d Spacings (A)	Relative Intensity (I/I_0)	hkl (I)	hkl (II)
2.15	14	(400)	(410, 322)
2.13	7		
2.01	7		(331)
1.984	4		(420)
1.971	7		
1.934	14	(420)	(421)
1.902	11		
1.883	22		(332)
1.862	14		
1.839	22	(332)	
1.804	26		(422)
1.695	7	(510, 431)	(511, 333)
1.633	4		(520, 432)

Structure	a_0 (A)
I BCC	8.65
II Simple Cubic	8.83

INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 1002°C (Cr-RADIATION)

d Spacing (A)	Relative Intensity (I/I_0)	hkl (I)	hkl (II)
7.79	8		
6.14	8	(110)	
4.42	19		(200)
4.35	8	(200)	
3.63	60		(211)
3.53	100	(211)	
3.44	24		
3.28	8		
3.24	19		
3.12	12		
3.07	12	(220)	
2.73	58	(310)	
2.69	48		
2.65	48		(311)
2.62	38		
2.58	19		
2.56	30		(222)
2.49	19	(222)	
2.45	12		(320)
2.41	24		
2.37	24		(321)
2.31	27	(321)	
2.27	27		
2.16	12	(400)	
2.12	15		
2.05	15		

(Continued)

INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 1002°C (Cr-RADIATION)

d Spacing (A)	Relative Intensity (I/I_o)	hkl (I)	hkl (II)
2.01	4	(411, 330)	
1.974	8		(420)
1.971	15	(420)	(421)
1.902	15		
1.883	15		(332)
1.862	8		
1.839	15	(332)	
1.829	15		
1.806	15		(422)
1.763	8	(422)	
1.695	15	(510, 431)	
1.672	8		
1.632	4		(520, 432)

Structure	a_o(A)
I BCC	8.64
II Simple Cubic	8.84

INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 1029°C (Cr-RADIATION)

d Spacing (A)	Relative Intensity (I/I_0)	hkl (I)	hkl (II)
7.75	7		
7.53	7		
6.31	7		(110)
4.42	10		(200)
4.32	10	(200)	
3.94	13		(210)
3.86	7		
3.78	17		
3.67	23		
3.62	39		(211)
3.52	100	(211)	
3.43	20		
3.40	10		
3.23	34		
2.91	17		(300)
2.78	10		(310)
2.73	63	(310)	
2.69	30		
2.64	30		(311)
2.62	56		
2.55	17		(222)
2.52	3		
2.50	17	(222)	
2.45	20		(320)
2.40	10		
2.37	34		(321)

(Continued)

INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 1029°C (Cr-RADIATION)

d Spacing (A)	Relative Intensity (I/I_o)	hkl (I)	hkl (II)
2.31	30	(321)	
2.26	21		
2.15	10	(400)	
2.12	20		
2.08	7		(411)
2.06	7		
2.05	23		
1.981	10		(420)
1.967	10		
1.934	17	(420)	(421)
1.902	20		
1.881	10		(332)
1.841	13	(332)	
1.829	13		
1.809	13		
1.802	13		(422)
1.787	7		
1.765	13	(422)	
1.743	3		
1.695	17	(510, 431)	
1.671	17		
1.633	7		(520, 432)

Structure	a_o (A)
I BCC	8.65
II Simple Cubic	8.85

INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 1047°C (Cr-RADIATION)

d Spacing (A)	Relative Intensity (I/I_0)	hkl (I)	hkl (II)
7.75	6		
7.53	6		
6.50	6	(110)	
4.42	6		(200)
4.31	12	(200)	
3.94	18		(210)
3.86	6		
3.77	24		
3.67	24		
3.61	21		(211)
3.52	100	(211)	
3.40	12		
3.23	30		
2.91	18		(300)
2.78	12		(310)
2.73	67	(310)	
2.69	21		
2.66	18		(311)
2.62	58		
2.55	12		(222)
2.50	27	(222)	
2.45	21		(320)
2.40	9		
2.37	30		(321)
2.31	33	(321)	
2.26	18		

(Continued)

INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 1047°C (Cr-RADIATION)

d Spacing (A)	Relative Intensity (I/I_o)	hkl (I)	hkl (II)
2.15	9	(400)	(410, 322)
2.12	21		
2.08	9		(411, 330)
2.06	6		
2.05	18		
1.981	12		(420)
1.967	9		
1.931	15	(420)	(421)
1.902	15		
1.881	3		(332)
1.843	9	(332)	
1.829	12		
1.809	6		
1.800	9		(422)
1.787	6		
1.763	12	(422)	(500, 430)
1.741	9		
1.695	12	(510, 431)	(511, 333)
1.671	12		
1.633	3		(520, 432)

Structure	a_o (A)
I BCC	8.65
II Simple Cubic	8.85

INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 1090°C (Cr-RADIATION)

d Spacing (A)	Relative Intensity (I/I_o)	hkl
3.61	12	
3.53	88	(211)
3.06	5	(220)
2.74	100	(310)
2.64	7	
2.31	65	(321)
2.27	7	
1.931	33	(420)
1.843	14	(332)
1.763	9	(422)
1.695	25	(510, 431)
1.578	9	(521)

Structure	a_o (A)
I BCC	8.66

INTERPLANAR SPACINGS AND INTENSITY MEASUREMENTS FOR SULFURIZATION PRODUCTS FORMED AT 1115°C (Cr-RADIATION)

d Spacing (A)	Relative Intensity (I/I_0)	hkl
3.53	78	(211)
3.06	5	(220)
2.73	100	(310)
2.31	64	(321)
1.931	30	(420)
1.841	20	(332)
1.763	8	(422)
1.693	22	(510, 431)
1.576	5	(521)

Structure	a_0 (A)
B.C.C.	8.65

INTERPLANAR SPACINGS AND INTENSITY MEASURFMENTS FOR SULFURIZATION PRODUCTS FORMED AT 1300°C (Cr-RADIATION)

d Spacing (A)	Relative Intensity (I/I_o)	hkl
3.53	77	(211)
3.06	5	(220)
2.73	100	(310)
2.31	72	(321)
1.931	30	(420)
1.841	22	(332)
1.763	10	(422)
1.693	28	(510, 431)
1.576	5	(521)

Structure	a_o (A)
B.C.C.	8.63

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